

Quasi-1D Physics in Breathing Metal-Organic Frameworks

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Introduction

Metal-organic frameworks (MOFs) present a class of materials showing properties akin to both solids and molecular systems. They consist of inorganic metal or metal-oxide clusters (nodes) connected through organic molecules (linkers), giving rise to porous, highly tunable frameworks. Their porous nature, with internal surface areas of $>1000 \text{ m}^2\text{g}^{-1}$, and chemical tunability, through the choice of nodes and linkers, makes them versatile materials that are receiving a rapidly growing interest with a large focus on industrial, chemically oriented processes, such as catalysis, gas separation and gas storage.

In this work, we focus on MOFs with the MIL-47 topology (*cf.* Fig. 1), which contain 1D transition-metal (TM) oxide chains. These MOFs belong to the class of so-called breathing MOFs because they can reversibly switch between a large-pore (LP) and narrow-pore (NP) configuration under the influence of guest molecules, temperature or pressure. The presence of transition metals on the other hand make these MOFs of interest for magnetic and/or multiferroic applications. We have studied the mechanical and electronic properties of such MOFs using *ab initio* methods, and found these MOFs to present an interesting test bed for quasi-1D physics.

Results and Discussion

In case of the MIL-47(V) MOF, the unit cell used contains 4 TM sites, which contain a single unpaired electron. This leads to 2^4 possible configurations of which 5 are inequivalent (*cf.* Fig. 2).

For each of these 5 configurations we fully optimized the structure. [1] The final atomic structures are nearly indistinguishable, and the calculated Hirshfeld-I charges [2,3] on the vanadyl chains show only very small variations between the different spin configurations. In contrast, the calculated mechanical properties (*cf.* below) vary strongly, showing these very small variations to be of importance.

The inter- and intra-chain coupling of the unpaired electrons is investigated by mapping the obtained *ab initio* energies onto a simple Ising-spin model showing that both interaction couplings are anti-ferromagnetic, although the inter-chain coupling is 2 orders of magnitude smaller than the intra-chain coupling. This shows that the TM oxide chains can be regarded as quasi-1D systems. [4]

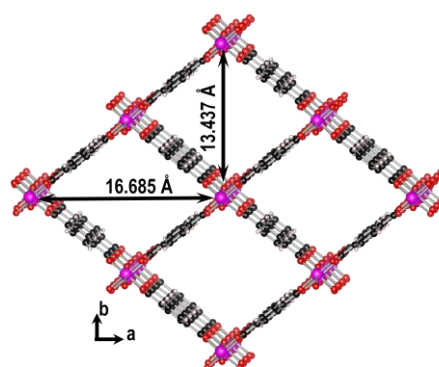


Figure 1: Ball-and-stick representation of the LP MIL-47 MOF.

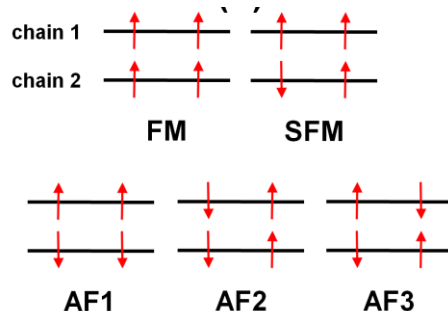


Figure 2: 5 inequivalent spin configurations

For the optimized structures also the bulk-modulus and its pressure derivative are calculated, and from these we derive a transition pressure at which the MOF is expected to show a phase-transition from the LP to the NP geometry (*cf.* Fig 3). Interestingly, it was found that the different spin configurations give rise to a clearly different bulk modulus of 6 GPa for ferromagnetic chains and 8 GPa for anti-ferromagnetic chains. This means that under a strong magnetic field the MIL-47(V) becomes softer. Also the transition pressure varies significantly: from 82 MPa to 124 MPa for the ferromagnetic and anti-ferromagnetic chains, respectively. [4] This is in perfect agreement with the pressure range, of 85 up to 125 MPa, observed in Hg intrusion experiments. [5] This shows that for polycrystalline samples, there may be a relation between the crystallite size and the fraction of ferromagnetic chains in the crystallite.

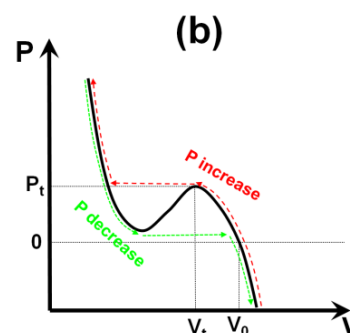


Figure 3 Schematic representation of pressure induced breathing.

Conclusions

In this first principles study of the MIL-47 breathing MOFs, we have shown that the TM oxide chains behave as quasi-1D systems. The spin configuration plays an important role in the system stability, although the system geometry is barely modified. Ferromagnetic and anti-ferromagnetic chains give rise to clearly different mechanical properties, which provides us fundamental understanding regarding the experimentally observed broad range of transition pressures during pressure induced breathing.

References

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